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The Photophysical Behavior of Ester-Substituted Aminocoumarins:
A New Twist

by

Gary B. Schuster and J. A. Van Gompel

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Abstract: The fluorescent behavior of two amino-substituted coumarin esters was examined in solvents of different polarity. Coumarin 3, a simple ester derivative, behaves conventionally. Its fluorescence emission shifts to lower energy as the solvent polarity increases and the efficiency of the emission is essentially unaffected by solvent change. This behavior is characteristic of a rotation-inhibited intramolecular charge transfer (ICT) state. Coumarin 4, substituted with an α-keto ester function at the 3-position, also shows emission characteristic of an ICT state. However, in this case, the fluorescence efficiency and lifetime of the excited state decrease markedly as the solvent polarity increases. This behavior is characteristic of formation of a non-emissive twisted intramolecular charge transfer (TICT) state. Since rotation of 4 about the carbon-nitrogen bond is inhibited, twisting must occur around another group in the molecule. Consideration of the structure leads to identification of a rotation around the bond connecting the carbonyl groups of 4 as leading to a TICT state.

The unusual dual fluorescence of p-N,N-dimethylaminobenzonitrile was first reported by Lippert[1] in 1962. Additional observations by Grabowski and co-workers led to their formulation of the twisted intramolecular charge transfer (TICT) hypothesis in 1973[2]. According to the current version of this theory, electronic excitation of the aminobenzonitrile chromophore leads to fluorescence from its lowest energy ^1L_b state in competition with a rotation around the carbon-nitrogen bond that generates an emissive, lower-energy TICT state[3]. Strong support for this proposal is found in studies of compounds whose structural features inhibit the necessary rotation. In these cases, TICT formation does not occur and only emission from the ^1L_b state is observed. Similarly, the separation of charge required by TICT theory has been confirmed by experiments which show that the dipole moment of the emissive, twisted state is much larger (ca. 12 D) than that of the ground state. Despite several challenges[4], the TICT approach continues to provide a satisfactory model that accommodates the experimental results on the photophysical properties of dimethylaminobenzonitriles.

Many additional substances are postulated to follow the TICT pattern set by the aminobenzonitriles. Among the well-studied examples of these are the aminocoumarins. Part of the motivation for the investigation of these compounds is their utility as laser dyes[5]. Jones and co-workers examined extensively the medium effects on the photophysical properties of aminocoumarin dyes 1 and 2 (Chart I)[6]. They found that the response of the fluorescence yields and lifetimes of these dyes to changes in solvent polarity is a sensitive function of the substitution pattern. Two important features were suggested to control the response. First, the low-lying emissive excited state of the aminocoumarins is postulated to be intramolecular charge-transfer (ICT) in character. The emission maxima for such states will shift to lower energy as the polarity of the solvent is increased. This effect is understandably larger for the trifluoromethyl-substituted examples since the degree of charge transfer is enhanced by the electron withdrawing substituent. Second, the activation barrier for conversion of the emissive ICT state to a non-emissive TICT state of the aminocoumarin decreases as the solvent polarity increases. This hypothesis is supported by the observation that the emission maxima for

rotation-prevented aminocoumarins 2a and 2b shift to lower energy with increasing solvent polarity, but that their fluorescence efficiencies and lifetimes are hardly affected by solvent change.

Rettig and Klock present a related hypothesis to explain the anomalously weak and red-shifted fluorescence of 6-aminocoumarin[7]. They argue that the high dipole moment of the emitting state identifies it as TICT with full charge separation. Similarly, Chu and Yangbo conclude from a recent study of the solvent polarity dependent behavior of aminocoumarins that TICT state formation is determined only by the electron accepting and donating character of the molecule[8].

In connection with our investigation of the chemiluminescence of coumarin derivatives[9], we had occasion to prepare and study the photophysical properties of formally rotation-inhibited aminocoumarins 3 and 4, Chart I. Ester-substituted coumarin 3 closely follows the pattern of behavior set by its related compounds described above. But α-dicarbonyl-substituted coumarin ester 4 is anomalous. We report herein the results of an investigation of the solvent-dependent photophysical properties of 3 and 4. Our findings indicate formation of a new sort of TICT state from 4.

Chart I
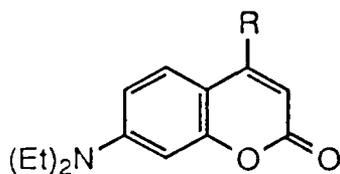
1a: R = CH$_3$
1b: R = CF$_3$
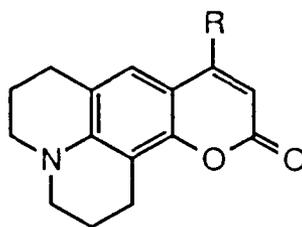
2a: R = CH$_3$
2b: R = CF$_3$
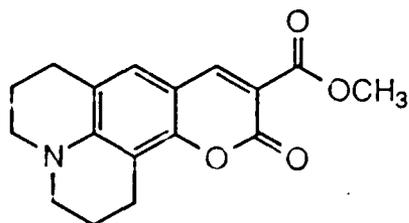
3
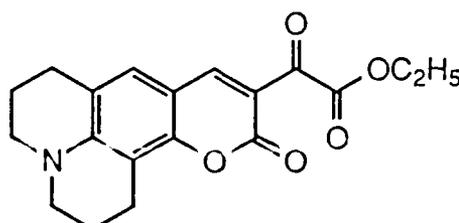
4

Results

The normalized electronic absorption spectra of dilute solutions (2×10^{-6} $\underline{M}$) of coumarins $\underline{3}$ and $\underline{4}$ in cyclohexane and in ethanol are shown in Figure 1; the extended chromophore of $\underline{4}$ is evident from the lower energy of its transition. Both compounds behave similarly to the change in solvent polarity; their absorption maximum shift to the red, 940 cm^{-1} for $\underline{3}$ and 990 cm^{-1} for coumarin $\underline{4}$, and their absorption bands broaden. Absorption maxima for the coumarins in other solvents are listed in Table I. The absorption spectra of coumarins $\underline{3}$ and $\underline{4}$ show an unusual dependence on concentration in cyclohexane but not in ethanol solution. When the concentration of the coumarins in cyclohexane is raised ca. 100 fold to 10^{-4} $\underline{M}$, a new, weak, broad absorption band with a maximum at ca. 22,720 cm^{-1} is detected in the spectrum. We attribute the new band to aggregates formed by self-association of the coumarins.

The fluorescence spectra of the two aminocoumarin esters in dilute cyclohexane or tetrahydrofuran (THF) solution are shown Figure 2. It is clear that the emission spectra of the two esters are closely related to each other. Coumarin $\underline{3}$ has an emission maximum at 23,150 cm^{-1} in cyclohexane solution which shifts red to 21,640 cm^{-1} in THF solution. Dicarbonyl coumarin ester $\underline{4}$ emits at 21,640 cm^{-1} in cyclohexane and this band shifts 1600 cm^{-1} to the red when the solvent is changed to THF. The Stokes loss in cyclohexane solution for coumarin $\underline{3}$ is 780 cm^{-1} and that for $\underline{4}$ under these conditions is 760 cm^{-1}. Emission maxima for these two coumarins in other solvents are listed in Table I. It is apparent from inspection of the data that the optical behavior of coumarins $\underline{3}$ and $\underline{4}$ are nearly identical.

The emission data reported in Table I can be analyzed by means of Lippert's equation[10] to probe the dipole moment difference between the coumarins in their ground and excited states ($\Delta\mu=\mu_e-\mu_g$); the results are shown in Figure 3. With the conservative assumption that the Onsager a parameter for these two coumarins is approximately the same, this analysis indicates that the changes in dipole moment for both $\underline{3}$ and $\underline{4}$ are nearly identical and that they are quite large for both compounds. This finding is consistent

with assignment of the origin for the emissive transition for both coumarin esters to an intramolecular charge transfer state of the same kind identified by Jones and co-workers[6] for the simpler coumarin derivatives 1 and 2.

The parallel behavior for coumarin esters 3 and 4 so readily apparent in the data described above does not extend to the solvent dependence of their emission efficiencies. The fluorescence quantum yields for the aminocoumarin esters were determined in a range of solvents by comparison with the known emission efficiency of the laser dye Coumarin 343 in ethyl alcohol solution[5]. The results are reported in Table I. In cyclohexane, a non-polar solvent, both coumarin esters fluoresce efficiently - ca. 100 and 85% for 3 and 4 respectively. The fluorescence efficiency of 3 is only slightly affected by changes in solvent polarity; it emits with 86% efficiency in ethyl alcohol. In striking contrast, the fluorescence efficiency of dicarbonyl coumarin ester 4 is remarkably sensitive to solvent polarity. In benzene solution its emission yield is 37%, in chlorobenzene the yield decreases to only 6%, and in ethyl alcohol no emission at all can be detected from 4. Evidently, there is a solvent dependent non-radiative decay path available to the ICT state of 4 that coumarin 3 does not possess.

The contrasting behavior of 3 and 4 can also be observed in the response of their excited state lifetimes to the change in solvent polarity, Table I. The lifetime measurements in cyclohexane solution are complicated by the self-association phenomenon noted earlier. But, as expected, the fluorescence lifetime of coumarin 3 is essentially unaffected by the solvent, and the fluorescence lifetime of coumarin 4 decreases dramatically as solvent polarity increases.

Discussion

The photophysical behavior of ester 3 is easily understood by analogy with other amino-substituted coumarins. The lowest singlet excited state of this substance is polar and highly emissive[10]. The response of the excited state to solvent change permits its characterization as having an ICT electronic configuration. Normally the ICT state of such compounds relax to lower energy, generally non-emissive TICT states by rotation about

the amino group carbon-nitrogen bond when such motion is possible. In the case of ester
3, this rotation is prevented and, characteristically, its emission efficiency is hardly
affected by the nature of the solvent.

The photophysical properties of dicarbonyl ester 4 requires a new sort of TICT state.
Both the similarities and the differences in the behavior of 3 and 4 are informative. As
with 3, the data indicate that the lowest excited singlet state of 4 has an ICT electronic
configuration; the emission from this state moves to lower energy in parallel with that
from ester 3. However, in contrast to the behavior of 3, the emission efficiency of 4
decreases markedly as the solvent polarity increases. Conventionally, this behavior
signals operation of a relaxation channel of the ICT state to a non-emissive TICT state.
This is unexpected for coumarin 4 since the normally required rotation about the
carbon-nitrogen bond is not possible. Clearly, if we are to maintain the ICT-TICT
paradigm that serves so well in so many cases, a twist about a different bond must be
assigned.

Scheme I

ICT
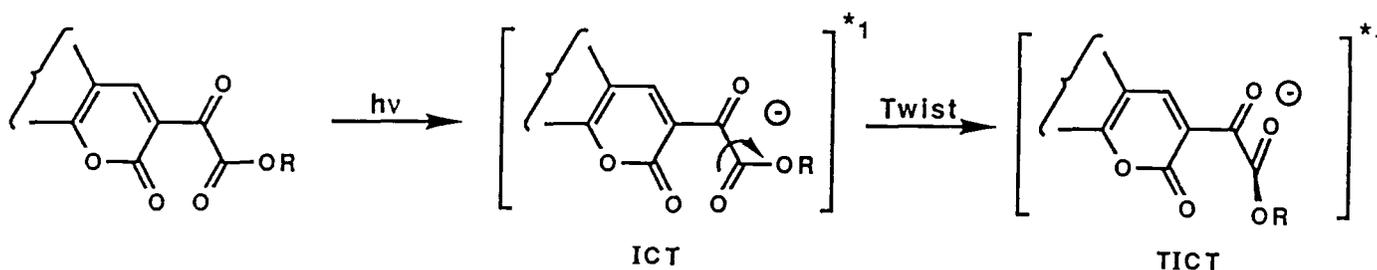
TICT

Consideration of the structure of esters 3 and 4 leads readily to the hypothesis that
relaxation from an ICT to the TICT state occurs by rotation about the bond joining the two
carbonyl groups of 4. Maximum overlap and conjugation in the ground states of coumarin
esters 3 and 4 requires that the carbonyl group and the coumarin ring have a co-planar
orientation. Support for this assertion is found by comparison of the absorption spectrum
of coumarin 2a with that of ester 3. The significant structural difference between these
two compounds is the ester substituent at the 3-position. This change causes the

absorption maximum of $\underline{3}$ in ethanol solution to shift 3580 cm^{-1} further red than that of

$\underline{2a}$. If the ester carbonyl group was not co-planar, or nearly so, with the coumarin ring,

it would not exert so large an effect on the absorption spectrum of $\underline{3}$. Similarly,

examination of the reported X-ray crystal structures for α-keto esters[12] reveals that the

dihedral angle between the carbonyl oxygen atoms is highly variable, ranging from a nearly

syn-planar arrangement in a methyl glyoxylate[12a] derivative to anti-planar for an

aliphatic keto ester[12b]. The strong structural dependence of this angle probably signals

a relatively shallow potential for rotation. Thus, it is reasonable to explain the

unusual photophysical properties of $\underline{4}$ by assigning a planar or nearly planar configuration

to its emissive ICT state and postulating that a rotation within the dicarbonyl group to a

non-planar orientation of the oxygen atoms gives a non-emissive TICT state, Scheme I.

Conclusions

The lowest excited singlet states of coumarins $\underline{3}$ and $\underline{4}$ have ICT electronic

configurations. The fluorescence efficiency of $\underline{3}$ is unaffected by solvent polarity but

that of $\underline{4}$ decreases markedly as the solvent polarity increases. This behavior is

attributed to the formation of a new sort of TICT state from $\underline{4}$ by rotation about the bond

connecting its two carbonyl groups.

Experimental Section

α-Ketocoumarin ethyl ester ($\underline{4}$). The precursor
9-formyl-8-hydroxy-2,3,6,7-tetrahydro-1H,5H-benzo[ij]-quinolizine[13] (2.0 g, 9 mmol) was

dissolved in 20 mL of acetonitrile in a 50 mL round-bottomed flask which was equipped with

a reflux condenser. Piperidine (1.0 mL, 10 mmol, 1.1 eq., distilled from NaOH pellets

before use) and diethyloxaloacetate (DOA, 1.0 g, 5.3 mmol, 0.6 eq.) were added to this

solution. The reaction mixture was heated at reflux over a steam bath and DOA (5.2 equiv)

was added in 1.0 g aliquots over of 5 d. The mixture turned very dark, and the reaction

was monitored by silica gel TLC; $\underline{4}$ could be seen as a red spot with an R_f – 0.2 using 5%

ethyl acetate in benzene as eluant. When DOA could no longer be seen by NMR spectroscopy

(singlet, 6.0 ppm), about 12 h after addition of the last aliquot, the more volatile components were removed under reduced pressure. Ester $\underline{4}$ was separated from the reaction mixture by MPLC using benzene on silica, and was crystallized from benzene/hexane solution to give 382 mg (12%) glistening red needles, m.p. 151-154°C. ^{1}H NMR (CDCl$_3$): δ8.28 (s, 1 H); 6.97 (s, 1 H); 4.42 (q, 2 H); 3.39 (m, 4 H); 2.85 (t, 2 H); 2.76 (t, 2 H); 1.98 (m, 4 H); 1.40 (t, 3 H). IR (CHCl$_3$): 1724, 1661, 1620, 1517, 1446, 1308, 1167 cm^{-1}. Analysis (C$_{19}$H$_{19}$NO$_5$): Calculated: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.87; H, 5.76; N, 4.03.

Fluorescence Efficiencies. Fluorescence efficiencies of methyl ester $\underline{3}$ and ethyl ester $\underline{4}$ were determined as follows. A solution of Coumarin 343 was prepared in chloroform having an absorbance > 0.10 at 448 nm. The Φ_{fl}, was determined by direct comparison with an ethanol solution of Coumarin 343 having a similar absorbance[5]. A solution of ester $\underline{3}$ or $\underline{4}$ in a chosen solvent was prepared and diluted until the absorbance maximum for the ester solution was the same as that of the chloroform solution of Coumarin 343. The fluorescence emission spectra for both solutions were recorded with the excitation wavelength set at the wavelength where their absorbance spectra were identical to eliminate the need to correct for the spectral output of the excitation lamp.

Fluorescence Lifetimes were measured by the phase delay and modulation method. Solutions of the esters were prepared in the chosen solvent so that the absorbance at 442 nm was less than 0.10. The samples were irradiated with the 442 nm line from a helium-cadmium laser which was modulated with a Pockel's cell. An aqueous solution of Ficoll (Sigma) was used as the blank for zero lifetime. Scatter was eliminated from the sample by removing all light below 480 nm using a UV cut-off filter. Data were taken at 1, 5, 10, 20, 30, 50, 80, 100, and 150 MHz and were analyzed using the ISS 178 software package.

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Table 1. Photophysical data for esters **3** and **4**.

	Coumarin 3				Coumarin 4			
	Absorption	Emission			Absorption	Emission		
Solvent	λ_{max} (nm)	λ_{max} (nm)	ϕ_f	τ_f (ns)	λ_{max} (nm)	λ_{max} (nm)	ϕ_f	τ_f (ns)
cyclohexane	418	435	1.0	4.4 (1.8)[a]	449	460	0.85	2.6
CCl$_4$					455	473	0.72	2.6
(i-C$_3$H$_7$)$_2$O	422	446	1.0	2.8	450	476	0.63	2.8
Benzene	425	456	0.85	2.8	456	487	0.37	2.0
THF	423	463	1.0	2.9	465	497	0.04	0.35
C$_6$H$_5$Cl	430	465	0.88	2.8	472	500	0.06	0.35
CHCl$_3$	435	465	0.89		474	500	0.04	0.052
CH$_2$Cl$_2$	436	470	0.82		473	505	<0.01	
CH$_3$CN	434	480	0.76		475		0	
C$_2$H$_5$OH	436	480	0.86		469	510	<0.01	

[a] The two components of the fluorescence decay may be a consequence of the self-association in cyclohexanes; due to its low extinction at 442 nm, concentrated solutions were used in the lifetime measurement.

Captions for Figures

Figure 1. Absorption spectra for coumarins **3** and **4** in cyclohexane and ethanol solutions at different concentrations. Curves are, starting from the left:

  i - dotted; coumarin **3**, dilute in cyclohexane
  ii - dot-dash; coumarin **3**, concentrated in cyclohexane
  iii - dash; coumarin **3**, dilute in ethanol
  iv - solid; coumarin **3**, concentrated in ethanol
  v - dotted; coumarin **4**, concentrated in cyclohexane
  vi - dot-dash; coumarin **4**, dilute in cyclohexane
  vii - coumarin **4**, concentrated in ethanol
  viii - solid; coumarin **4** dilute in ethanol.

Figure 2. Fluorescence emission spectra for couramins **3** and **4** cyclohexane and THF solution: A - coumarin **4** in THF; B - coumarin **4** in cyclohexane; C - coumarin **3** in cyclohexane; D - coumarin **3** in THF.

Figure 3. Lippert plots for coumarins **3**, circles, and **4**, triangles.

Absorbance

Wavelength (nm)

Emission Intensity

Wavelength (nm)